Chapter Three

Integrated Studies of the Surface Ocean and Air-Sea Interface

3.1 Overview

A comprehensive observing system of sea surface pCO_2 distributions and air-sea CO_2 fluxes will greatly enhance our understanding of the carbon cycle and its anthropogenic perturbations. In this chapter, we recommend a series of studies to dramatically extend our knowledge of the distribution of pCO_2 values at the sea surface, and of the fluxes of CO_2 between ocean and atmosphere. We recommend process studies of gas exchange to improve the characterization of air-sea CO_2 fluxes. We also recommend large-scale measurement of upper ocean properties that reflect and constrain biogeochemical transports and fluxes. This work will improve our knowledge of the nature and rates of biogeochemical processes. It will also improve our ability to characterize the surface pCO_2 field by advancing our ability to quantify these rates. The timescale of interest is seasonal to interannual, and the primary spatial scales of interest are sub-basin to basin.

The upper ocean studies recommended here complement studies recommended in the chapters on atmospheric observations (Chapter 2) and ocean interior measurements (Chapter 4). These other chapters advocate powerful approaches to constraining atmospheric and oceanic CO_2 inventories on large space scales and multiyear timescales. The measurements proposed here will offer insights about air-sea CO_2 fluxes on subregional and seasonal scales, as well as at larger scales of space and time. Knowledge of air-sea CO_2 fluxes as constrained by sea surface pCO_2 measurements will also give powerful information for modeling, leading to more accurate CO_2 uptake estimates by the land biosphere at continental scales. Systematic observations of seasonal changes in sea surface pCO_2 and ancillary properties (e.g., O_2, nutrients, TCO_2, isotopes, dissolved organic matter) yield information about instantaneous and integrated rates of biological carbon transformations in the mixed layer. Measurements of mixed layer $\delta^{13}C$ of dissolved CO_2, in particular, are important for estimates of terrestrial CO_2 uptake and net oceanic production (Francey *et al.*, 1995; Keeling *et al.*, 1995; Ciais *et al.*, 1995; Battle *et al.*, 2000). Sea surface pCO_2 measurements will contribute to be a basic long-term goal: making independent observations from the atmosphere, surface ocean, and ocean interior that yield consistent CO_2 flux measurements, without having to invoke "missing" sources and sinks. Studies recommended here will thus contribute to many priority objectives of the U.S. Carbon Cycle Science Plan (CCSP).

This chapter advocates the following long-term strategy and goals for characterizing the time-dependent distribution of pCO_2 in the surface ocean, gas transfer velocities and air-sea fluxes, and the biogeochemical processes determining the large-scale pCO_2 distribution:

- Making extensive measurements of the distribution of sea surface pCO_2 and related biogeochemical properties, to map the variations of these properties in time and space.
- Interpreting these data (1) to achieve a deeper understanding of upper ocean biogeochemical processes, and (2) to quantify their impact on sea surface pCO_2 distributions. This work will involve integrating observations made with satellite-borne sensors, results of biogeochemical process studies, and models of ocean physics and biogeochemistry.
- Carrying out process studies to improve parameterizations of gas transfer velocities in terms of environmental forcing, giving more accurate values of air-sea CO_2 fluxes determined from sea surface pCO_2 values.
- Integrating results from the observation systems (including satellites), associated databases, gas exchange parameterizations, and models of upper ocean biogeochemistry and physics to calculate surface water pCO_2 and air-sea CO_2 fluxes at seasonal timescales and regional spatial scales, in near real time. This last exercise serves as a framework to upscale results to the global scale in the future.

The plan proposed here focuses on measurements in the open ocean, and may not incorporate all important components of the oceanic carbon sink. The coastal oceans are an unknown, but possibly significant, sink for carbon. The land-ocean pathway through rivers delivers about 0.6 Pg C/yr to the ocean. This pathway will receive attention in the RIOMAR program (`http://www.tulane.edu/~riomar/workshop.htm`). This plan does not discuss in detail satellite observations, which offer unparalleled synoptic coverage of parameters that influence surface CO_2 levels and gas transfer rates. These parameters include wind speed, sea surface temperature, and ocean color (from which values for chlorophyll and primary productivity can be derived). Satellite fields of these data will contribute fundamental information to sea surface studies. An outline of these capabilities is provided in Appendix F. NASA carbon planning activities (`http://www.earth.nasa.gov/visions/researchstrat/research_strategy.htm`) address coastal observations and satellite observations.

To lay the foundation for fulfilling the objectives above, we present a plan for a 5-year program with two broad goals. The first goal is to determine climatological air-sea CO_2 fluxes on seasonal timescales and achieve greater biogeochemical understanding of factors controlling pCO_2 in priority ocean basins. The second is to improve measurement technologies, advance modeling skills, and extend our knowledge of ocean pCO_2 and flux variations. In this way we will also acquire the information to plan for a comprehensive sea surface pCO_2 observing system 5 years hence. These objectives are now becoming tractable thanks to recent advances in measurement techniques, and because remote sensing offers synoptic coverage of key properties.

An obvious way to characterize air-sea CO_2 fluxes is by direct measurement. In fact, achieving this ability has been a major recent advance in carbon cycling studies (Fairall, 2000). However, such measurements are too

demanding for global or regional coverage. Rather, air-sea CO_2 fluxes must be constrained using two terms. The first is the pCO_2 difference between air and surface seawater, ΔpCO_2. The second is the gas transfer velocity, which converts the pCO_2 gradient to flux. Constraining these terms at the basin scale is problematic. Sea surface pCO_2 is highly variable in time and space. Gas transfer velocities need to be parameterized in terms of some widely characterized property of the sea surface, such as satellite estimates of wind speed or wave slope. Such parameterizations are currently not well constrained. They must be significantly improved to accurately calculate air-sea gas fluxes. We separate the discussion and recommendations on sea surface pCO_2 studies from those on determining gas transfer velocity.

This report proposes a 5-year ramp-up program with the following general objectives:

1. Design and implement an observing system for sea surface pCO_2 observations to improve climatological estimates of air-sea CO_2 fluxes for regions where added data will significantly improve continental and oceanic constraints. Studies should cover the global ocean, with a focus on the North Atlantic, equatorial Pacific, North Pacific, and Southern oceans.

2. Gain the required experience with various platforms and sensors, and improve our analytical capabilities, including standardization and instrument development, so that we can begin a comprehensive program to constrain basin-scale interannual variability to ±0.1–0.2 Pg C/year, 5 years hence.

3. Make observations aimed at achieving process-level understanding of (a) space scales and timescales of sea surface pCO_2 variability, which define the frequency of observations required for accurately constraining interannual variability on a basin scale, and (b) physical and biological processes influencing pCO_2 variations between observations. This work will involve measuring ancillary biogeochemical properties as well as pCO_2 itself, and will require close coordination with process studies of ocean biology and physics.

4. Improve our understanding of gas exchange parameterizations and scaling, so that we can accurately calculate CO_2 fluxes from air-sea pCO_2 differences.

5. Establish data and modeling systems so that results are accessible to all interested users.

3.2 Background

Fluxes of CO_2 across the air-sea interface are commonly determined from the bulk formula:

$$FCO_2 = ks(pCO_{2a} - pCO_{2w}) = ks\Delta pCO_2 \tag{3.1}$$

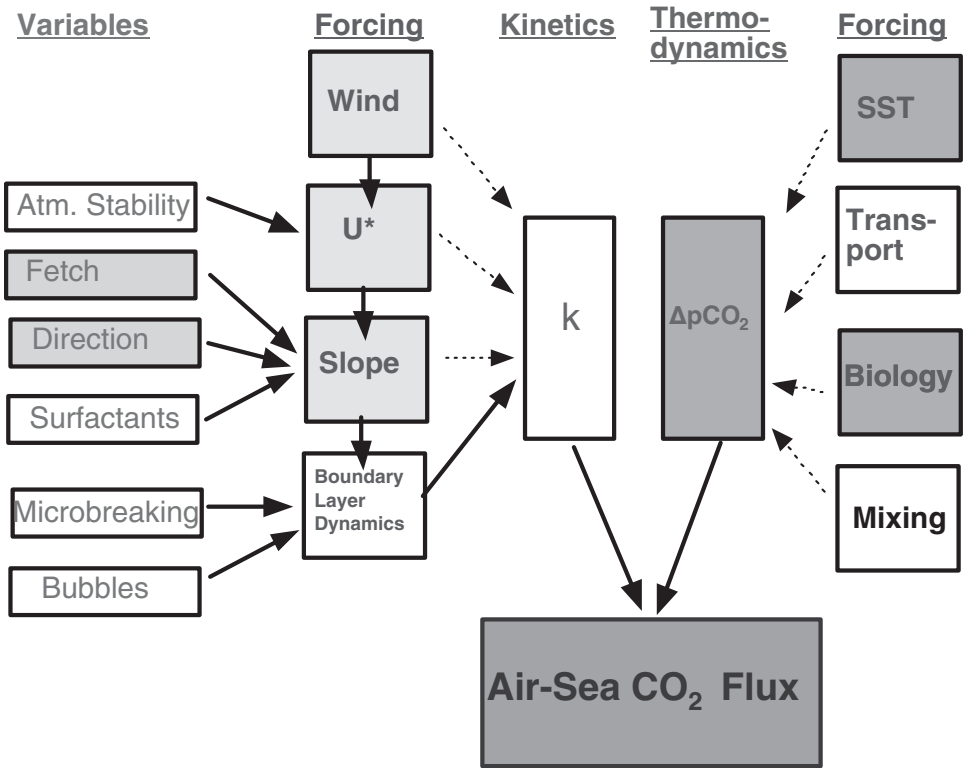

Figure 3-1: Factors influencing air-sea CO_2 fluxes, broken down into those that influence k and those that influence ΔpCO_2 (SST, sea surface temperature).

where FCO_2 is the flux (mol m^2/yr), k is the gas transfer velocity (m/yr), s is the solubility (mol/m^3/atm), and pCO_{2a} and pCO_{2w} are the partial pressures of CO_2 (atm) in air and water, respectively.

The product of the gas transfer velocity and the solubility (ks) is sometimes referred to as the gas exchange coefficient. The ΔpCO_2 is the thermodynamic driving force, while the gas transfer velocity is the kinetic term. Both terms must be quantified to constrain the air-sea flux. Figure 3-1 illustrates the processes that influence each term. As the figure indicates, a complex set of variables controls the fluxes at small scale. To quantify regional fluxes, the controlling properties must be understood and parameterized.

This chapter deals independently with our current knowledge of the sea surface pCO_2 field and gas exchange parameterizations, and approaches for studying these properties. We start by summarizing information about the climatological sea surface pCO_2 field and basin/global scale fluxes. A discussion about characterizing gas transfer velocities follows. We then discuss issues associated with making a more detailed characterization of the sea surface pCO_2 field, including the relevance of biogeochemical processes. The section ends with a discussion of network design, based on analysis of existing sea surface pCO_2 data.

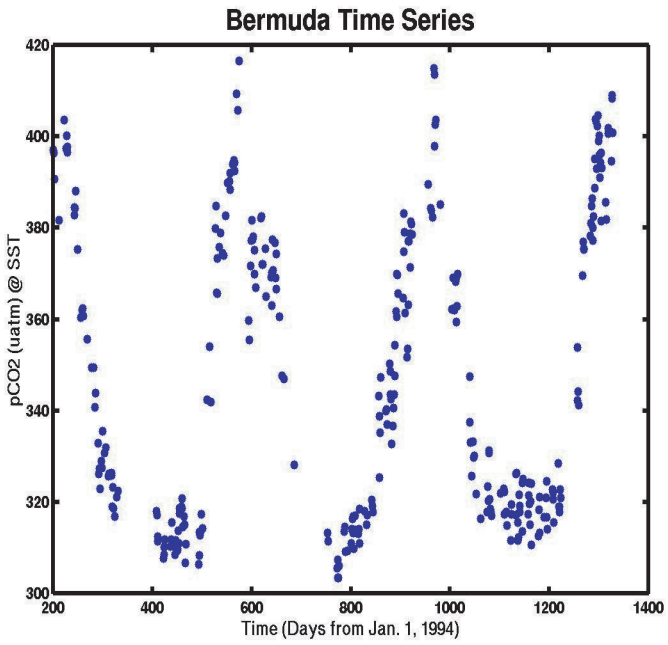

Figure 3-2: Temporal variation of surface water pCO_2 observed in the vicinity of the BATS site (31°N, 64°W), observed from mid-1994 through early 1998 by N. Bates (BBRS; Bates, 2001).

3.2.1 Studies of sea surface pCO_2 and climatology of air-sea fluxes

A major effort has gone into mapping the distribution of pCO_2 at the sea surface and determining air-sea CO_2 fluxes using gas exchange rates obtained from wind speed. The data are sufficiently extensive that we can now estimate monthly climatological air-sea CO_2 fluxes by ocean basin, if sometimes with a large uncertainty.

The partial pressure of CO_2 (pCO_2) in surface ocean waters was first measured over the global ocean with sufficient precision (± 3 μatm) in 1957–1960, as part of the International Geophysical Year (Takahashi, 1961; Keeling, 1968). This work successfully documented the large-scale pattern of sea surface pCO_2 variations: (1) warm equatorial waters are a strong source for atmospheric CO_2; (2) cold subpolar and polar waters are often a strong sink for CO_2; and (3) temperate oceans are nearly in equilibrium with atmospheric CO_2.

During the following 40 years, over a million pCO_2 measurements have been made in surface ocean waters of the global ocean. These measurements include data on waters sampled underway along ship tracks as well as several important time series. Long time series at Bermuda (Bates, 2001) (Fig. 3-2), Station "P" (Wong and Chan, 1991) (Fig. 3-3), and Iceland and the French KERFLUX Station in the Kerguelen Islands (Louanchi *et al.*, 2001) constrain seasonal rates of net production, as well as seasonal to interannual changes in pCO_2. The Japanese Meteorological Agency has maintained a

program of repeated measurements along 137°E in the eastern North Pacific between the equator and 38°N, during January–February of each year since 1984. Detailed sea surface pCO_2 fields are being measured in the equatorial Pacific using both a volunteer observing ship (VOS) and moorings. These data reflect the degassing rate of this important region, as well as interannual variability of air-sea fluxes resulting from El Niño. Table 3-1 provides a summary of several major surface observational programs.

These efforts notwithstanding, the oceans remain seriously undersampled in time and space (Fig. 3-4). Except for the time-series sampling described above, information on interannual variability in sea surface pCO_2 is sparse. Extratropical manifestations of ENSO (El Niño/Southern Oscillation) are uncharacterized. Large-scale climate reorganizations such as the Pacific Decadal Oscillation (PDO) or the North Atlantic Oscillation (NAO) could affect air-sea fluxes of CO_2 by changing wind regimes, sea surface temperatures (SSTs), biological productivity, and ecosystem structure. There are almost no data for some large reaches of the ocean, such as most of the South Pacific. The current monthly climatology of pCO_2 was produced by T. Takahashi and colleagues from a synthesis of the available data (Takahashi *et al.*, 1997, 1999, and 2001). Sea surface pCO_2 values are expressed as monthly climatological values on a $4° \times 5°$ grid for the global ocean. These researchers' approach illuminates three continuing challenges to our efforts.

The first involves creating a climatology for a transient signal. The ΔpCO_2 values have to be calculated for a single virtual year from data collected over several decades. The sea surface pCO_2 during recent decades rose at the atmospheric rate in a subtropical region (Bermuda Atlantic Time Series, BATS), but did not increase with time in boreal and polar regions (Station P and Iceland). The regional pCO_2 observations were normalized according to these observed trends, thereby projecting data collected over several decades to a single virtual year. Second, the data cover periods of different oceanic states, notably including both El Niño and La Niña. Equatorial Pacific data collected during El Niño years were excluded. Still unresolved are questions about the extratropical response to El Niño, the influence of the NAO on sea surface pCO_2 fields, and the contribution of El Niño itself to surface wind fields. Third, the ocean remains seriously undersampled in time and space even after collapsing all the data onto a single year. Takahashi and collaborators dealt with inadequate spatial and temporal sampling by placing data into $4° \times 5°$ grid fields and used sea surface current fields from a transport model and data for nearby areas to estimate pCO_2 values for unsampled points on the grid. Basin and global scale fluxes of CO_2 between the atmosphere and oceans (Fig. 3-5) are summarized in Table 3-2; the uncertainty caused by interannual variations and use of different wind-speed products is expressed in Table 3-3. Errors in ΔpCO_2 that lead to an uncertainty of ± 0.1 Pg C/yr in air-sea carbon fluxes are summarized by basin in Table 3-4.

Table 3-1: Summary of ongoing observations of sea surface biogeochemical properties.

Ship	Type	Group	Line	Frequency	Funding Source	Status	Notes
Ron Brown	research	Wanninkhof/Feely	random	1 Eq. Pac. cruise/yr	NOAA/OGP	year 2 of 3 funding	pCO_2, chl, [DIC & O_2]
Ka'imimoana	research	Feely/Wanninkhof	Eq. Pac. (East of 160°E)	2 × year	NOAA/OGP	year 2 of 3 funding	pCO_2
Voyager of the Sea	cruise ship VOS	Wanninkhof	Miami-Caribbean	1 × week	NOAA/OAR	starting up 2001	pCO_2, chl, ADCP
Skaugran	cargo ship VOS	Nojiri	Japan-West Coast America	1 × month	Japan Science Agency	1995–2000	pCO_2, chl, nutrients, Alk, DIC & O_2
Alligator Hope	cargo ship VOS	Nojiri	Japan-West Coast America	1 × month	Japan Science Agency	2000 onward	pCO_2, chl, nutrients, Alk, DIC & O_2
Supply ship	cargo/research	Lefèvre/Watson	UK-Falklands	1 year	UK	1996 onward	pCO_2, chl
Supply ship	cargo/research	Metzl	S. Indian	2 × year	France	1996 onward	pCO_2 chl
Palmer	research	Takahashi/Sweeney	New Zealand/Antarctica	4 × year	NOAA/OGP	1998–2000	pCO_2
Palmer	research	Takahashi/Sweeney	New Zealand/Antarctica	4 × year	NSF	2001 onward	pCO_2
Gould	research	Takahashi/Sweeney	Chile-Antarctica	8 × year	NSF	2001 onward	pCO_2
Tulley	research	Wong/Degrandpre	Vancouver-Sta. P	4 × year	Canada	2000 onward	pCO_2, chl, Alk, DIC, & O_2
Polarstern	research		N. Atlantic-Antarctic	1 × year	German		pCO_2
Falstaff	cargo ship VOS	Körtzinger	Germany/Canada	1 × month	funded	2001 for 3 years	pCO_2
Nuka Arctica	cargo ship VOS	Johannessen	Denmark/Greenland	1 × month	funded	2001 for 3 years	pCO_2
City of London	cargo ship VOS	Lefèvre	UK-Caribbean	1 × month	funded	2001 for 3 years	pCO_2
Hesperides	research	Rios	Spain-Antarctica	2 × year	funded	2001 for 3 years	pCO_2
Polar Star	Coast Guard	Wanninkhof/Feely	W. Coast Antarctica	2 × year	planned	2001 for 1 yr	pCO_2
Oleander	cargo ship VOS	Bates		24 × year	planned		pCO_2/ADCP/XBT
American Star	cargo ship VOS	Dickson/Robbins	W. Coast-Australia	1 × month	planned		air measurements (Tans/Bender)
Moorings							
Bermuda Test bed		Dickey, Degrandpre, Chavez, YSI				Current	pCO_2, NO_3, chl, radiation
Sta. P		Degrandpre, Wong				Planned	pCO_2
Eq Pac, 150°W, 170°W		Chavez, Friederich			NOAA/OGP	since 1996	pCO_2, NO_3, chl
Labrador Sea		Wallace, DeGrandpre			EU	5/00–5/01	pCO_2
Leo-15 (NJ)		DeGrandpre			NSF-OCE	1998–present	pCO_2
Buzzards Bay (MA)		McGillis, DeGrandpre			NSF	1999–present	pCO_2
Historical							
Baldrige	research	Wanninkhof/Feely	random		NOAA/OGP	1990–1996	pCO_2
Discoverer	research	Gammon/Feely	Pacific	1 × year	NOAA/OGP	1985–1995	pCO_2
APL	cargo VOS	Takahashi	N. Pacific	4–6 × year	DOE	1988–1992	pCO_2, ^{14}C, ^{13}C
TFL	cargo VOS	Takahashi	N. Atlantic	4–6 × year	DOE	1988–1992	pCO_2, ^{14}C, ^{13}C
Exxon Tanker	Oil tanker VOS	Garvey/Takahashi	Atlantic & Indian	4 × year	Exxon	1980	
	VOS	Wong	Pacific	4–6 × year		1986–90	pCO_2, nutrient
Knorr	research	Weiss	random			1978–1997	pCO_2, CH_4, N_2O
Melville	research	Weiss	random			1978–1997	pCO_2, CH_4, N_2O
Wecoma	research	Weiss	Hawaii Tahiti Shuttle	6 × year		1980	pCO_2, CH_4, N_2O

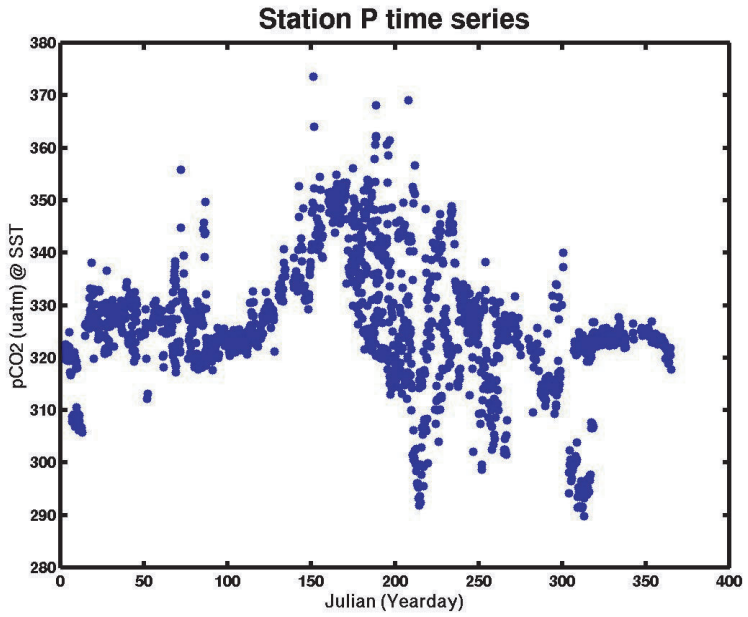

Figure 3-3: Seasonal variation of surface water pCO_2 and sea surface temperature (SST) observed at Station "P" (50°N, 145°W) in 1972–1975 (Wong and Chan, 1991). Note that SST changes are more or less sinusoidal, with a seasonal amplitude of 8°C, while surface water pCO_2 does not exhibit a simple sinusoidal pattern, changing only by 50 μatm, rather than the 130 μatm that might be expected from a 8°C change.

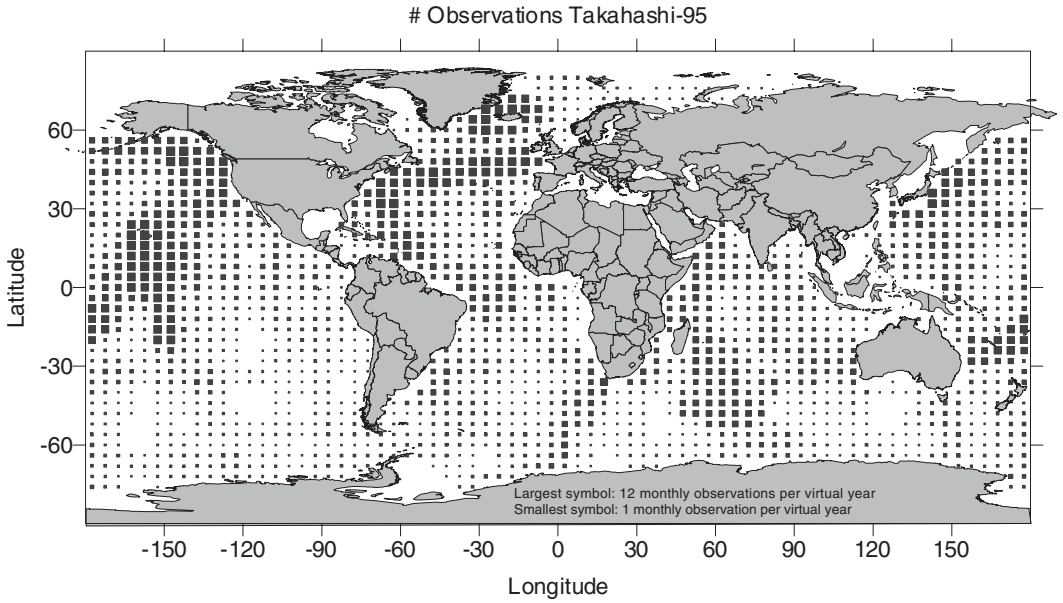

Figure 3-4: Schematic of number of monthly observations taken in each $4° \times 5°$ grid box. The largest square denotes 12 months of coverage in a virtual year.

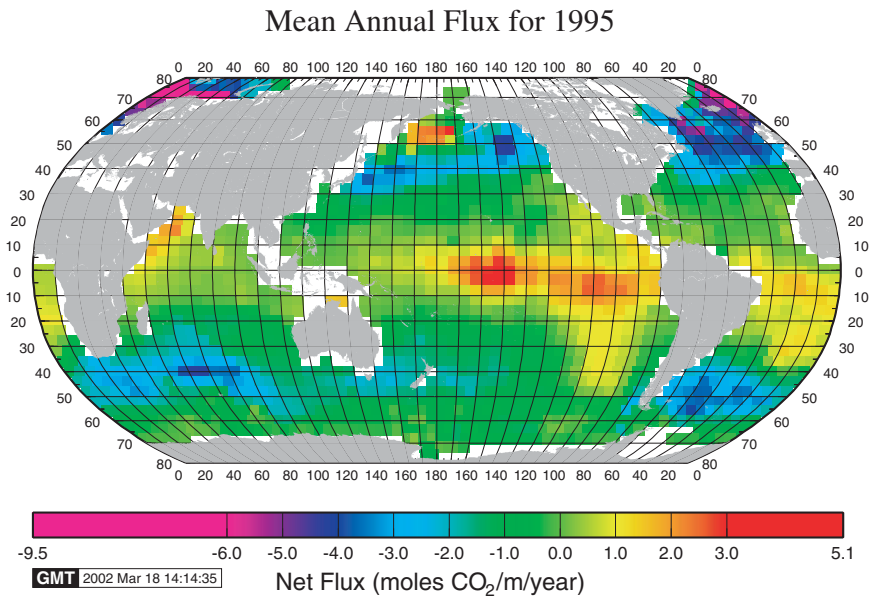

Figure 3-5: Net air-sea CO_2 flux over the globe, (wind speed)^2—from Wanninkhof (1992).

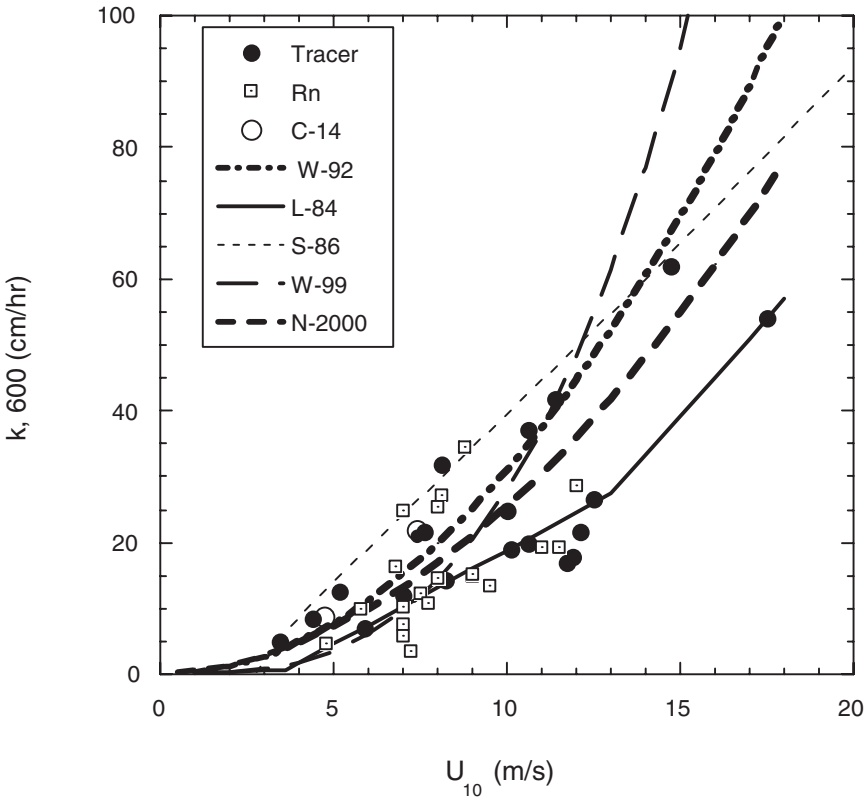

Figure 3-6: Summary of gas exchange results in the ocean and empirical relationships derived in part from this data. All data have been normalized to Sc = 600. Tracer: dual-tracer results; Rn: ^{222}Rn results; C-14: global estimate based on bomb-radiocarbon. The empirical relationships are those of Liss and Merlivat (1983) (L-83), Wanninkhof "steady winds" (1992) (W-92), Smethie *et al.* (1986) (S-86), Wanninkhof and McGillis "steady winds" (1999) (W-99), and Nightingale *et al.* (2000) (N-2000).

Table 3-2: Comparison of regional fluxes*.

Lat. Band	ΔpCO_2 Data	Gas Transfer Coefficient	Pacific Ocean	Atlantic Ocean	Indian Ocean	Southern Ocean	World Ocean
N of 50°N	T-01	W-92	+0.01	−0.40	—	—	−0.39
	T-99	W-92	−0.02	−0.48	—	—	−0.49
	T-01	W&M-99	+0.03	−0.55	—	—	−0.52
14°N–50°N	T-01	W-92	−0.64	−0.34	+0.07	—	−0.92
	T-99	W-92	−0.62	−0.32	+0.06	—	−0.87
	T-01	W&M-99	−0.94	−0.48	+0.10	—	−1.31
14°N–14°S	T-01	W-92	+0.74	+0.15	+0.18		+1.07
	T-99	W-92	+0.73	+0.18	+0.15	—	+1.06
	T-01	W&M-99	+0.67	+0.14	+0.20	—	+1.00
14°S–50°S	T-01	W-92	−0.51	−0.33	−0.67	—	−1.51
	T-99	W-92	−0.48	−0.27	−0.79	—	−1.54
	T-01	W&M-99	−0.68	−0.51	−0.97	—	−2.16
S of 50°S	T-01	W-92	—	—	—	−0.47	−0.47
	T-99	W-92	—	—	—	−0.59	−0.59
	T-01	W&M-99	—	—	—	−0.74	−0.74
Oceanic Regions	T-01	W-92	−0.40	−0.92	−0.43	−0.47	−2.22
	T-99	W-92	−0.39	−0.88	−0.58	−0.59	−2.44
	T-01	W&M-99	−0.92	−1.39	−0.67	−0.74	−3.72
Regional Flux (%)	T-01	W-92	18	41	19	21	100
	T-99	W-92	16	36	24	24	100
	T-01	W&M-99	25	37	18	20	100
Area	(10^6 km^2)	—	151.6	72.7	53.2	31.7	309.1
	(%)	—	49.0	23.5	17.2	10.2	100

*Based on the Takahashi climatology (Takahashi *et al.*, 1999) and a recent update (Takahashi, 2001). Two different parameterizations of gas exchange and wind speed are used—Wanninkhof (1992) (W-92), and Wanninkhof and McGillis (1999) (W&M-99)—illustrating the effect of the different parameterizations. In this analysis, the NCEP 41-year averaged wind-speed product is used. However, if NCEP winds for 1995 are utilized, the global uptakes of –2.22, –2.44, and –3.72 in the last column of "oceanic regions" change to –1.95, –2.06, and –2.97 Pg/yr, illustrating the sensitivity to wind speed. Moreover, if the 6-hour NCEP winds are used rather than monthly winds, the –2.96 Pg/yr (W&M-99) drops to –2.34 Pg/yr (Wanninkhof *et al.*, 2001—from Feely *et al.*, 2001).

3.2.2 Parameterizing Gas Transfer Velocities for Calculating Air-Sea Fluxes

Determining ΔpCO_2 and k on appropriate time and space scales

As noted above, direct CO_2 flux measurements, based on observations of very small CO_2 gradients in the air immediately above the ocean surface, can only be performed on dedicated oceanographic process cruises. Moreover, k and ΔpCO_2 are affected by different factors on different timescales (Fig. 3-1). Large-scale CO_2 fluxes are therefore determined from experimental measurements of ΔpCO_2, together with parameterized values of k (Fig. 3-1).

Calculating the mean air-sea fluxes by simply averaging k and ΔpCO_2 on arbitrary time and space scales, and computing their product, gives incorrect values. The error arises because of the cross-correlation between the parameters, and also because of the nonlinearity of the gas exchange–wind-speed relationship. The average flux can be expressed as:

$$F_{av} = (ks\Delta \mathrm{pCO}_2)_{av} = (ks)_{av}\Delta \mathrm{pCO}_2)_{av} + ((ks)'\Delta \mathrm{pCO}_2')_{av} \qquad (3.2)$$

where "av" is the averaged quantity over a specified timescale.

The term $(ks)_{av}$ is not simply related to the mean wind because of the nonlinear dependence of k and u. The cross-correlation term $((ks)'\ \mathrm{pCO}_2')_{av}$ accounts for the correlation between the two quantities. The magnitude of the cross-correlation term is poorly constrained. For instance, at high winds the cross-correlation is caused by increasing gas transfer velocities and mixed layer deepening. These changes can lead to entrainment of either high or low pCO_2 waters into the mixed layer depending on season, euphotic zone depth, and mixed layer depth. Nonlinearity in the gas transfer velocity can lead to biases on the order of 30% if monthly averages are used rather than hourly quantities. Regional fluxes must therefore be derived from a robust extrapolation scheme that takes temporal and spatial variability of k and $\Delta \mathrm{pCO}_2$ into account. Global satellite observations of wind and surface roughness from scatterometer and altimeters will lead to improved determinations of gas transfer velocity. Remotely sensed sea surface temperature (SST) and ocean color will also lead to a better understanding of patterns of sea surface pCO_2 variability.

Measurements of k

To obtain accurate regional fluxes, we must be able to relate the gas transfer velocity to environmental forcing and obtain regional estimates of k on the timescale of the variability in forcing (hours). This involves improving techniques to measure k. We also need a better understanding of the controls on k. Possible artifacts and biases must be assessed, and results must be validated/verified by independent approaches. Achieving these advances will require dedicated field efforts and measurements on platforms of opportunity.

Until recently, the gas transfer velocity was determined exclusively from indirect measurements based on mass balance techniques in the surface mixed layer. The techniques utilized natural or deliberate tracers that yielded gas transfer velocities averaged over periods of days to weeks (Lapitan *et al.*, 1999; Nightingale *et al.*, 2000). The successful improvement of direct flux techniques now makes it possible to measure the flux and determine k from collocated $\Delta \mathrm{pCO}_2$ measurements, on the timescale of variability of forcing (of order 1 hour). Algorithms relating gas exchange to wind speed are developed either from compilations of field data (Nightingale *et al.*, 2000), controlled studies at a single field or laboratory site (Watson *et al.*, 1991), or a combination of field and laboratory data (Liss and Merlivat, 1986). Several recent gas exchange models are constrained by budgets of radiocarbon in the ocean (Wanninkhof, 1992; Wanninkhof and McGillis, 1999). Radiocarbon is also used as a constraint or validation of global ocean biogeochemistry models so that such parameterizations facilitate consistent observation and model-based results. Data from past field experiments are insufficient for

Table 3-3: The effects of wind speeds and of the wind-speed dependence of the CO_2 gas transfer coefficient on the net sea-air CO_2 flux using the climatological sea-air pCO_2 difference obtained in this work*.

		Pg C/yr					
Lat. Band	**Gas Transfer Wind Data**	**Pacific Ocean**	**Atlantic Ocean**	**Indian Ocean**	**Southern Ocean**	**Global Ocean**	**Errors in Flux**
N of 50°N	W-92/41-yr	+0.01	−0.40	—	—	−0.39	+28%, −23%
	W-92/1995	+0.03	−0.18	—	—	−0.14	
	W&M-99/41-yr	+0.03	−0.55	—	—	−0.52	+44%, −35%
	W&M-99/1995	+0.07	−0.17	—	—	−0.10	
14°N–50°N	W-92/41-yr	−0.64	−0.34	+0.07	—	−0.92	+25%, −23%
	W-92/1995	−0.29	−0.28	+0.03	—	−0.54	
	W&M-99/41-yr	−0.94	−0.48	+0.10	—	−1.31	+43%, −32%
	W&M-99/1995	−0.29	−0.38	+0.02	—	−0.64	
14°N–14°S	W-92/41-yr	+0.74	+0.15	+0.18	—	+1.07	+29%, −24%
	W-92/1995	+0.61	+0.07	+0.15	—	+0.83	
	W&M-99/41-yr	+0.67	+0.14	+0.20	—	+1.00	+43%, −31%
	W&M-99/1995	+0.62	+0.05	+0.12	—	+0.79	
14°S–50°S	W-92/41-yr	−0.51	−0.33	−0.67	—	−1.51	+22%, −20%
	W-92/1995	−0.57	−0.31	−0.50	—	−1.38	
	W&M-99/41-yr	−0.68	−0.51	−0.97	—	−2.16	+37%, −30%
	W&M-99/1995	−0.88	−0.51	−0.63	—	−2.02	
S of 50°S	W-92/41-yr	—	—	—	−0.47	−0.47	+26%, −21%
	W-92/1995	—	—	—	−0.58	−0.58	
	W&M-99/41-yr	—	—	—	−0.74	−0.74	+41%, −32%
	W&M-99/1995	—	—	—	−1.02	−1.02	
Oceanic Regions	W-92/41-yr	−0.40	−0.92	−0.43	−0.47	−2.22	+22%, −19%
	W-92/1995	−0.21	−0.69	−0.33	−0.58	−1.81	
	W&M-99/41-yr	−0.92	−1.39	−0.67	−0.74	−3.72	+40%, −32%
	W&M-99/1995	−0.48	−1.01	−0.48	−1.02	−3.00	
Regional Flux (%)	W-92/41-yr	18	41	19	21	100	
	W-92/1995	12	38	18	32	100	
	W&M-99/41-yr	25	37	18	20	100	
	W&M-99/1995	16	34	16	34	100	

*The flux values have been computed using the (wind speed)^2 dependence of the CO_2 gas transfer coefficient by Wanninkhof (1992) (W-92) and the (wind speed)^3 dependence of this coefficient by Wanninkhof and McGillis (1999) (W&M-99), respectively, for each of the two sets of wind data: the NCEP/NCAR 41-year and 1995 mean monthly wind speeds. Errors in flux (expressed as percentage of the flux) in the far right column represent the flux changes resulting from plus or minus one standard deviation (about ± 2 m sec^{-1} on the global average) from the annual mean wind speed in each pixel area. The positive errors in the flux represent when the mean monthly wind speed over each pixel area was increased by one standard deviation; the negative errors represent when the mean wind speed was reduced by one standard deviation (Takahashi *et al.*, 2001).

deriving authoritative parameterizations of gas transfer velocities. Part of the problem is that measurements and forcing scales are not aligned.

Broecker *et al.* (1986) expressed a number of concerns about attempts to measure gas exchange rates in oceanic conditions. Fairall *et al.* (2000) demonstrated important technical improvements that now allow such measurements. Advances in direct flux measurement techniques, and airside gradient and covariance measurements, have decreased the temporal scale to hours and spatial scale to below 1 kilometer. Successful examples include the ocean-atmosphere direct covariance method for CO_2 (McGillis *et al.*, 2001a; McGillis *et al.*, 2001b) and the gradient method for DMS (dimethylsulfide) (Dacey *et al.*, 1999; McGillis *et al.*, 2001b). The ability to measure k

Table 3-4: Mean annual sea-air pCO_2 difference, annual flux, and sea-air pCO_2 required for 0.1 Pg C flux*.

Ocean Region	Average ΔpCO_2 (μatm)	Ocean Area (10^6 km^2)	ΔpCO_2 per 0.1 Pg C (per yr uptake)	Annual Flux (Pg C/yr)
Northern North Atlantic	−47.4	7.45	11	−0.39
Temperate North Atlantic	−9.3	23.95	6	−0.27
Equatorial Atlantic	+19.9	15.43	14	+0.13
Temperate South Atlantic	−3.1	26.08	4	−0.24
Polar South Atlantic	−26.4	7.10	11	−0.22
Northern North Pacific	−8.8	4.45	20	−0.02
Temperate North Pacific	−10.0	43.04	3	−0.47
Equatorial Pacific	+29.67	50.19	4	+0.64
Temperate South Pacific	−7.4	53.05	3	−0.36
Polar South Pacific	−9.0	17.44	4	−0.20
Temperate North Indian	+35.9	2.12	132	+0.03
Equatorial Indian	+14.0	21.05	14	+0.10
Temperate South Indian	−20.0	30.49	4	−0.57
Polar South Indian	−10.1	7.16	10	−0.10
Global Oceans		308.99		−1.94

*All values are for the reference year 1995. The wind-speed data of Esbensen and Kushnir (1981) and wind-speed dependence of the gas transfer coefficient of Wanninkhof (1992) have been used.

locally in the field now provides the tools to properly relate the gas transfer to the appropriate forcing function. However, wind parameterizations will continue to be used extensively in the near future, both because wind is an important driver of surface turbulence controlling gas transfer, and because synoptic measurements and assimilation products of wind speed are readily available. Improvements in these parameterizations, especially in our ability to apply the relationships over appropriate time and space scales, will improve flux estimates.

Future work must be geared toward characterizing the near surface turbulence that controls gas transfer. Capillary waves are closely related to turbulence, and k is strongly affected by these waves (Bock *et al.*, 1999). Moreover, capillary waves generate a large return on scatterometers that are in orbit to measure global winds on daily timescales. The initial work suggests that k is more closely related to the scatterometer return than the winds derived from the return. Parameterizing k in terms of scatterometer return promises an improvement in the algorithms used to estimate k (Wanninkhof and Bliven, 1991; Frew *et al.*, 1999).

3.2.3 Studies of Biogeochemical Fluxes at the Sea Surface: Climatology and Interannual Variability

Sea surface pCO_2 and Upper Ocean Biogeochemisty

Sea surface pCO_2 is the second term determining air-sea CO_2 fluxes. While gas transfer velocities are determined by wind speed or sea surface roughness,

sea surface pCO_2 is regulated by biogeochemical processes and fluxes in the upper ocean. In principle, we can characterize sea surface pCO_2 fields from observations alone, perhaps with the aid of simple interpolation schemes. Interpolating in the context of the physical circulation field (e.g., Takahashi *et al.*, 1999) will give improved results. We can derive still more accurate sea surface pCO_2 fields by utilizing biogeochemical models specifying carbon fluxes. The pCO_2 data themselves inform us about such models, because they reflect upper ocean biogeochemical fluxes controlling total dissolved CO_2 (TCO_2), total alkalinity (TA), and pCO_2 in the mixed layer.

A number of ancillary biogeochemical properties give complementary information about upper ocean carbon fluxes. We define "ancillary properties" as concentrations or isotopic compositions of solutes that constrain organic carbon fluxes, provided that water mixing and gas exchange rates are well constrained. Ancillary properties that constrain upper ocean net production include TCO_2 (Gruber *et al.*, 1998); TA; biological O_2 supersaturation, estimated from O_2 and Ar supersaturation (Wannikhof *et al.*, 1995; Emerson *et al.*, 1995; Luz and Barkan, 2000); nutrients (Sweeney *et al.*, 2000; Zhang *et al.*, 2001; Louanchi and Najjar, 2000); dissolved organic carbon (DOC); dissolved organic nitrogen (DON); dissolved organic phosphorous (DOP); and $\delta^{13}C$ of CO_2 (Zhang and Quay, 1997). $\delta^{15}N$ and $\delta^{18}O$ of nitrate reflect nutrient sources to the euphotic zone and nutrient utilization (Sigman *et al.*, 2000). The triple isotope composition of O_2 constrains gross photosynthetic O_2 production (Luz and Barkan, 2000). Utilizing these tracers will advance many aspects of our understanding of the quantitative influence of biogeochemical fluxes on pCO_2 of the mixed layer and air-sea CO_2 fluxes at various scales.

These properties constrain carbon fluxes only in the proper physical settings and are often not applicable. There are other high-priority biogeochemical properties whose study is being planned by other efforts. Iron, for example, is clearly a high-priority property that lies outside our mandate.

Below, we recommend systematic measurements of ancillary properties as an adjunct to the pCO_2 measurements themselves. These measurements will give information about net and gross euphotic zone production over broad reaches of the oceans. The results will allow us to build improved models of upper ocean physics/biogeochemistry, leading to more accurate interpolated sea surface pCO_2 fields. As well, net and gross production rates constrained by pCO_2 and ancillary properties will give mechanistic insights for improving prognostic models to calculate sea surface pCO_2 fields in future decades and centuries.

Among the ancillary properties, $\delta^{13}C$ of TCO_2 is of special interest. This property, when combined with atmospheric CO_2 and $\delta^{13}C$ measurements, yields estimates of anthropogenic CO_2 uptake rates by the land biosphere and the oceans (e.g., Francey *et al.*, 1995; Keeling *et al.*, 1995; Ciais *et al.*, 1995). A major limitation of this approach is insufficient sea surface $\delta^{13}C$ data. Geographical and seasonal coverage is limited. Time series data have been collected only at BATS and HOT, in subtropical gyres where seasonal variations are smaller than in eutrophic waters. Extended sea surface $\delta^{13}C$ measurements, recommended below, will reduce the uncertainty in the

air-sea $\delta^{13}C$ disequilibrium and significantly improve estimates of the CO_2 uptake rates based on atmospheric CO_2 and $^{13}CO_2$ budgets.

Studies of synoptic and seasonal variability in sea surface pCO_2

Below, we recommend two primary approaches for studying the variability of sea surface pCO_2: underway measurements on ships, and continuous measurements on moorings. Ship-based measurements give CO_2 variations over long oceanic lines. Measurements made on repeat transits also give information about seasonal variability. Data collected on ocean crossings give pCO_2 fields of waters covering different physical and biogeochemical provinces of the oceans.

Moorings give complementary information by informing us about variations in pCO_2 and other properties in response to physical forcing over five important timescales. The first is the timescale of synoptic events, which influence surface properties and biogeochemistry by driving vertical mixing. The passage of eddies, whose dynamics also influence biogeochemistry (Garcon *et al.*, 2001), occurs at a similar timescale. The second timescale of interest is seasonal. Physical forcing induces large changes in water column structure, nutrient supply, solar irradiance, and consequently biogeochemical dynamics due to the seasonal progression. In most regions, pCO_2 variations are largest at the period of a year (e.g., seasonal changes dominate the variability). The third timescale is the annual. This period is the basic unit for defining fluxes that are important with respect to anthropogenic carbon as well as transport into the ocean interior. The fourth timescale of interest is the interannual. Fifth and finally, of course, there is the decadal and longer timescale associated with global anthropogenic change. The latter two timescales are discussed next.

Ocean biogeochemistry and decadal variability

Above, we noted that two modes of temporal variability could influence biogeochemistry on decadal timescales: natural interannual variability, and long-term evolution of ecosystems driven by anthropogenic global change. There is considerable observational evidence for the former, and modeling evidence that the latter will eventually be important.

Natural interannual variability in biogeochemistry is driven by interannual and decadal changes in the coupled ocean-atmosphere system. The phenomena most relevant here are ENSO, the NAO, and the PDO. ENSO variations comprise the most intense mode of interannual variability. They have a correspondingly strong influence on ocean biogeochemistry. During ENSO years, upper ocean waters in the eastern equatorial Pacific are warmer, more stratified, and consequently lower in nutrients (Barber *et al.*, 1996; Strutton and Chavez, 2000). Biomass and primary production is correspondingly lower, and there are indications that net or new production is lower as well. Fisheries yields are suppressed.

Recent studies at HOT and BATS show that biogeochemical processes at both sites have varied in response to physical forcing associated mainly

with the Southern Oscillation Index (SOI) and the NAO, respectively. This work suggests the pervasiveness of interannual variability as well as its complexity. In the 1970s, there was a shift in the SOI, linked with greater water column stratification at HOT (Karl, 1999). Associated with this shift was a decrease in dissolved SiO_2 and reactive phosphate concentrations, an increase in chlorophyll concentrations, and an increase in productivity (Karl *et al.*, 2001). There was also a shift in the nature of primary producers, with prokaryotes replacing eukaryotes.

During the 1990s, there were two cycles of the NAO, manifested in surface water temperature variations at BATS (Bates, 2001). During cooler phases, stratification was weaker, nutrient concentrations in the upper ocean were higher, and productivity was higher than during warmer phases (Bates, 2001; Steinberg *et al.*, 2001). Steinberg *et al.* (2001) did not find compelling links between the physical forcing and other biogeochemical properties. Nevertheless, at BATS as well as HOT, interannual variability is accompanied by some changes in biogeochemistry. A provocative result of this combined work is that increased stratification at HOT and decreased stratification at BATS both lead to higher productivity.

Systematic interannual variations in climate affect much of the world's surface oceans. They induce variations in upper ocean temperature and mixing that clearly have the potential for biogeochemical consequences. In three regions studied sufficiently to date (BATS, HOT, and the equatorial Pacific), we do observe significant biogeochemical responses to this forcing. Additional long-term studies of physical forcing and biogeochemical responses can provide us with insights for quantifying biogeochemical fluxes and their effects on sea surface pCO_2. Two additional attributes make time series studies important for understanding the effects of global change on ecosystems, ecosystems' influence on sea surface pCO_2, and their effects on oceanic sequestration of anthropogenic CO_2. First, interannual variability is by far the natural mode of change that comes closest to simulating effects of anthropogenic global change, and is arguably the best modern study subject for determining effects of global change. Second, some modes of global change are likely to be amplifications of interannual variability. This may be the case for the tropical Pacific, where simulations suggest that global change will push the ocean toward mean conditions closer to one of the existing modes.

3.2.4 Constraints on network design

We examined optimal sampling strategies for sea surface pCO_2 through a network design study. The results allowed us to determine the feasibility of constraining regional air-sea fluxes at a given level of accuracy, and to configure an appropriate sampling network. Our general strategy for addressing this question was to determine the resolution of pCO_2 measurements needed for constraining regional ΔpCO_2 to yield a flux accurate to 0.1 Pg C/yr, assuming that the gas transfer velocity is perfectly known. We determined this resolution based on observations of pCO_2 measured continuously along

cruise tracks. Results are given in appendices to this document (Appendix D, Appendix E).

The results show that regional ΔpCO_2 values can be accurately characterized with a small number of sea surface pCO_2 samples, even when variability is large. For example, Sweeney *et al.* calculate that one needs to characterize ΔpCO_2 to ± 3 μatm in the temperate North Pacific to constrain the basin scale flux to ± 0.1 Pg C/year. They calculate that this ΔpCO_2 accuracy can be achieved by sampling at evenly spaced 400 km intervals nine times per year. This analysis suggests that regional fluxes could be constrained with a small number of discrete observations, but there remain several unresolved issues. A similar analysis by Sweeney *et al.* (2001, unpublished results) shows that the correlation-length scales for fluxes, in contrast to those for pCO_2, are 5-fold shorter. Limited discrete sampling would not give process level information on air-sea CO_2 fluxes or biological carbon transformations, hampering modeling and assimilation efforts. Thus, closer spacing is necessary, at least until the spatial and temporal variability can be properly characterized.

We believe that we can obtain better accuracy with an automated unit that measures pCO_2 of surface water samples continuously on ships. There is the added benefit of being able to characterize small-scale pCO_2 variability, which can then be investigated using data about concentrations and fluxes inferred from auxiliary measurements. The network design studies provide an important constraint on the resolution of continuous, parallel, zonal or meridional CO_2 lines required to calculate basin-scale fluxes. Required resolution for repeat VOS lines is $\sim$5–10°, depending on the basin and the precise objectives.

Autonomous sensors would greatly enhance our ability to observe the distribution of CO_2 and related properties in the oceans. Such instruments can be installed on a variety of platforms, such as moorings, moored profilers, floats, drifters, and gliders. They can then be used to make continuous measurements with little or no subsequent support. Currently, sensors are available or under advanced development to measure pCO_2, TCO_2, O_2, total gas pressure, nutrients, and particulate organic carbon (POC). As well, autonomous moored seawater collectors allow us to measure many of these properties, as well as trace metals and concentrations of other terms of interest. In addition, autonomous sensors measure critical biological properties that, while outside the scope of our planning, are relevant because they give critical information about biogeochemical processes in the upper ocean. These include chlorophyll and other bio-optical properties that allow us to continuously determine primary production. The combination of concentration and biogeochemical measurements on the same moorings will greatly enhance the significance of the results. Autonomous platforms and instruments are described in more detail in Appendix G.

3.3 Recommendations for Observations of Sea Surface pCO_2 and Related Properties

Surface water pCO_2 observations should have the overall goal of constraining and ultimately forecasting air-sea CO_2 fluxes on seasonal timescales. Reaching this goal requires a range of measurements from process-scale studies to autonomous measurements of pCO_2 on large scales. We thus envision a close relationship between process-oriented studies and the longer-term and larger-scale observing systems described here. The process-oriented studies must include investigations of biogeochemical and physical controls on sea surface pCO_2, and studies of the physical controls on gas transfer velocity. Biogeochemical process studies are being planned independently. However, this plan addresses the first-order need to accurately constrain gas transfer velocities using satellite-measured property fields. Remotely sensed data are an essential tool for scaling observations and process-level insights to ocean basins and the globe. They will also provide improved understanding of the controlling processes. We thus foresee a spectrum of studies, including dedicated research ships for process studies, research ships of opportunity with more extensive measurement capabilities, commercial VOS, and autonomous platforms.

Recommended programs are given priorities ranging from 1 (highest) to 3. The following recommendations define a 5-year plan and are described below roughly in order of priority. The proposed projects, priorities, and cost estimates can be found in tabular form in Table 3-5.

3.3.1 Form and improve international collaborations on unified data protocols and standardization (priority 1)

Significant efforts are underway in other nations and regions, most notably Japan, the EU, Canada, and Australia, to gather surface pCO_2 data. A summary of the EU plans can be found in Appendix H. Reciprocal arrangements should be negotiated with the foreign laboratories for a full exchange of data. Ideally, all data would be in a compatible format; but if not, foreign data should be modified for posting on the American website.

International collaborations should include the sharing of sampling and analytical protocols. Executing this objective successfully will require international workshops, assistance in setting up data reduction protocols, and perhaps provision of technical support and hardware. Estimated cost is $300,000 per year.

3.3.2 Measure pCO_2 and related properties on volunteer observing ships

The measurement of pCO_2 and related properties on VOS will provide the first-order data set for constraining air-sea fluxes of CO_2 and rates of biogeochemical processes that mediate sea surface pCO_2 values. Again, we note the particular importance of $\delta^{13}C$ of CO_2 among the ancillary properties. We recommend the following studies in the next 5 years.

Table 3-5: Priorities and cost estimates for surface observation program.

Element of the implementation plan	Priority	Ship time	Costs/year
Recommendations for the Next 1 to 5 Years*			
Form and improve international collaborations on unified data protocols	1		$300,000
Measure pCO_2 and related properties on volunteer observing ships			
VOS studies in the North Atlantic (4 ships)	1		$520,000
VOS studies in the Southern Ocean (existing/new 4 ships)	1/2		$600,000
VOS studies in the equatorial Pacific (2 ships)	1/2		$300,000
VOS studies in the equatorial and North Pacific (2 ships)	2		$600,000
Meridional trans-Atlantic and trans-Pacific lines (4 ships)	3		$150,000
Measurements of ancillary properties (5 ships)	1–5		$1,000,000
Improve our understanding of the physics of gas exchange			
Longer term observations	1		$750,000
Upscaling studies	2		$350,000
Process studies	3	$1,000,000	$1,500,000
Deploy moorings for time series of pCO_2 and related biogeochemical properties			
Time-series stations at HOT and BATS (including mooring)	1		$2,000,000
Equatorial Pacific time series (4 systems, excluding cost of moorings)	1		$600,000
Boreal time series in the North Atlantic and North Pacific (including mooring)	2	$1,000,000	$2,000,000
Time-series sites in the Southern Ocean (including mooring)	4	$1,000,000	$2,000,000
Design a data access system	2		$400,000
Develop improved autonomous sensors for sea surface analysis			
Develop improved autonomous sensors for sea surface analysis of pCO_2	2		$400,000
Develop for measurement of ancillary properties	3		$1,000,000
Develop formalisms for interpolating air-sea CO_2 fluxes in time and space	3		$300,000
Deploy drifters with pCO_2 sensors to map pCO_2 fields			
Southern Ocean drifters (20)	4	$1,000,000	$1,200,000
Subpolar/subtropical North Atlantic drifters (20)	4	$360,000	$1,200,000
Equatorial Pacific drifters (20)	4	$450,000	$1,200,000

*Results from years 1–5 will be used to plan for a comprehensive sea surface pCO_2 observing system 5 years hence as measurement technologies, modeling capabilities, and knowledge of ocean pCO_2 are improved.

Initiate VOS studies in the North Atlantic (priority 1)

We recommend that four commercial VOS that run repeat cruise tracks spanning the entire basin be instrumented to measure pCO_2 and ancillary properties. Ships should be chosen based on cruise track, likely stability on route, available scientific infrastructure (e.g., whether the ship has TSG, XBT, or ADCP operations), and access for maintenance. The primary scientific criterion for choosing cruise track should be to sample the North Atlantic waters that are now most seriously undersampled with respect to CO_2 fluxes. This criterion directs more attention to areas of large ΔpCO_2 and higher wind speeds. The work should be coordinated with a recently funded European effort (CAVASOO; see Appendix H). Estimated total cost for four ships is $520,000 per year.

Continue and initiate VOS studies in the Southern Ocean (priority 1 for continuing sampling studies, priority 2 for new sampling studies)

The Southern Ocean may be an important sink region for anthropogenic CO_2. It plays a large role in the global carbon cycle (Sarmiento *et al.*, 1998). Understanding biogeochemical dynamics here is particularly important because models consistently show the potential for anthropogenic effects to induce large changes (Sarmiento *et al.*, 1998; Matear *et al.*, 1999; Matear *et al.*, 2000). There is also a large discrepancy in the estimated magnitude of the Southern Ocean CO_2 sink based on atmospheric CO_2 distributions and fluxes calculated from the Takahashi climatology (Takahashi *et al.*, 1999; 2001). The VOS program for the Southern Ocean would involve a total of at least four ships. It should take advantage of both American ships and other nations' ships of opportunity. We particularly note the availability of scientific and resupply ships that operate regularly in the Southern Ocean. The program might also include commercial VOS running great circle routes in the Southern Ocean, or cruise ships, if either of these offer reliable and desirable cruise tracks. Here as elsewhere, we should encourage and assist in other national efforts, and plans should be made for data sharing. For example, the Australians have almost a decade's worth of data south of Australia but currently this program is under considerable financial stress. Total estimated cost for the four ships is $600,000 annually.

Continue VOS studies in the equatorial Pacific (priority 1)

The equatorial Pacific is an important region that accounts for a large part of the interannual variability in air-sea pCO_2 fluxes. Ongoing underway measurements of sea surface pCO_2 should continue in the equatorial Pacific using one or two scientific ships of opportunity operating in that region. Total estimated cost for the two ships is $300,000 per year.

Initiate VOS studies in the North Pacific (priority 2)

Four commercial VOS operating along repeat tracks in the North Pacific should likewise be instrumented for continuous measurements of sea surface pCO_2 and ancillary properties. Selection criteria for these ships should be similar to those for ships used in the North Atlantic. Total estimated cost is $600,000 per year.

Initiate meridional transects on ships of opportunity in the Atlantic and Pacific (priority 2)

Since the largest CO_2 gradients in air and water are observed in the north-south direction, and since there are large uncertainties in fluxes deduced from atmospheric inversion studies for South America and Africa, some meridional lines should be occupied. These lines should include atmospheric sampling of CO_2 and related isotopes and tracers. Lower cost will be realized by placing instruments on established VOS/XBT lines that have infrastructure already set up. Total cost is $150,000 per year for two ships.

Measure temperature, salinity, and ancillary biogeochemical properties (priorities 1–3, depending on property and cost)

Temperature and salinity need to be measured wherever pCO_2 is measured. Vertical profiles of T and S should be measured along lines where data on mixed layer thickness and water column stratification is particularly important to understand upper ocean chemistry and biogeochemical fluxes. Cost of thermosalinograph installation is approximately $40,000. XBTs can be obtained for $35 each. Whenever possible, VOS selection should be based on infrastructure already in place.

Ancillary biogeochemical measurements are of interest along all cruise tracks, and especially so in two cases. The first is where they provide information about seasonal biological processes that induce large seasonal variations in sea surface pCO_2. The second is where data on the distribution of chemical and biological properties can give important information about anthropogenic carbon fluxes as well as biogeochemical processes and their rates.

$\delta^{13}C$ of CO_2 in the mixed layer is considered priority 1, because it is a critical term when using $\delta^{13}C$ of atmospheric CO_2 to partition CO_2 uptake between the land biosphere and ocean. Other ancillary properties are provisionally assigned a priority that is one level lower than that of the CO_2 measurements in their respective ocean basins. Again, decisions need to be made in individual cases based on cost and scientific justification. Total estimated cost for ancillary properties (which do not include T and S) is $1 million annually.

3.3.3 Develop understanding of the physics of gas exchange, to improve our ability to parameterize gas transfer velocities using data collected from satellites; develop and test gas exchange parameterizations with eddy accumulation experiments (priorities 1–3)

The general approach for the CO_2 observation plan is to perform process-level studies of long duration (more than 1 year) to compare detailed measurements of the sea surface CO_2 flux field with air-sea fluxes using parameterized gas exchange velocities. These parameterizations will be based on wind speed and the surface wave field, inferred largely from buoy arrays and satellite retrievals of these properties. In this manner, the process and time-series studies can be scaled up from mesoscale to larger regions.

Our recommendations focus on scaling up process-level information to the larger scale, with the necessary validations at each step of the assimilation process. Doing so involves several development steps:

- *Collocate gas transfer velocity measurements with ocean-surface pCO_2 measurements.* Air-sea CO_2 flux estimates are only as good as the product of measurements of ocean surface pCO_2 and k. Conversely, information on spatial and temporal variability of surface pCO_2 is needed to compute accurate transfer velocities from direct CO_2 flux measurements.

- *Validate fluxes.* Simultaneously measure fluxes using independent approaches, because direct flux measurements are susceptible to biases. Specifically, implement direct air-sea flux measurements of CO_2 and other gases, and employ proxies such as mass balance approaches of radon and deliberate tracers. On larger scales, this includes independent constraints to determine whether regional air-sea gas fluxes are consistent with atmospheric measurements of O_2/N_2, $^{13}C/^{12}C$, and ^{13}C disequilibrium measurements between water and air.

- *Improve the accuracy of gas transfer velocities.* Target measurements to improve accuracy of calculated fluxes and understanding of controls. Time-series stations and stable platforms are particularly effective for carrying out long-term observations to improve quantification of air-sea CO_2 fluxes.

- *Improve algorithms for parameterizing gas transfer velocities.* Perform studies to improve parameterizations by adding measurements of air-sea CO_2 fluxes and controlling physical processes of the sea surface to those research cruises involved in ocean surface pCO_2 surveys. Conduct cruises to different regions to study spatial and seasonal variability.

- *Develop tools for spatial extrapolation.* We must utilize satellite products for remote sensing of gas transfer velocity, and possibly properties used to derive pCO_2, to be assimilated in models. Remotely sensed

products and surface ocean pCO_2 climatology should be made openly and readily available.

These goals must be implemented through three approaches: process studies to quantify fluxes and factors controlling the fluxes, longer term observations to determine flux variability, and studies to quantify the upscaling of local fluxes. *The distinction between process studies of gas exchange and longer duration studies is in the platform of choice and number of support measurements.* The longer-term observations would take place on fixed ocean platforms or dedicated ships, such as *SeaOrbiter*, which are stable and have well-characterized flow distortion profiles. The process studies are ship-based campaigns. They will be more exploratory and will include water column measurements to understand the processes controlling pCO_2.

The recommended gas exchange studies follow.

Carry out longer-term observations of gas exchange (priority 1)

Direct flux measurements must be performed to determine whether we can derive unique parameterizations for the gas transfer velocity, and to assess the impacts of episodic events such as storms on fluxes. Observations from fixed platforms and opportunistic research ship voyages are cost-effective. Initially, an easily accessible coastal observatory should be equipped, but eventually an open-ocean site should be selected to measure a range of fluxes. The French *SeaOrbiter* is a free-floating platform much like FLIP but for longer duration studies. It is one of the candidate platforms for opportunistic, extended flux studies in the open ocean. Research ships often perform direct flux measurements of heat and momentum that require the same equipment used to determine small-scale velocity fluctuations. These cruises should be augmented to measure CO_2 fluxes as well. Aside from measuring fluxes, accurate measurements should be taken of environmental forcing, such as friction velocity, wave slope, and surface turbulence parameters. Incorporating a remote-sensing component such as scatterometry is highly desirable. Estimated cost is $750,000 annually.

Perform upscaling studies (priority 2)

To calculate air-sea CO_2 flux fields, we need to quantify spatial and temporal variability in relevant properties from observations and satellite data. We then need to include this information, using statistical techniques, in the estimation of regional fluxes. Here we recommend support for experimental studies that will improve our ability to interpolate and extrapolate. Field observations should be supported to develop algorithms characterizing regional fluxes. Synthesis and modeling studies should include improved parameterizations using products that can be measured remotely. This requires incorporating spatial and temporal variability of surface parameters into regional flux estimates by statistical means to quantify variability as determined from satellites. Estimated cost is $350,000 per year.

Perform process studies of gas exchange (priority 3)

The two recently completed NOAA efforts, the GasEx 1998 and 2001 studies, have shown the feasibility of the direct flux measurements and have provided initial results on parameterization with forcing. Future studies should have a greater focus on parameterization using remotely sensed products. They should be collocated with intensive basin observations of ΔpCO_2. The recommendation is to perform one process study each in the North Atlantic, North Pacific, and Southern Ocean areas during a period when VOS are intensely studying the sea surface pCO_2 field. The estimated cost (per process study) is \$1.5 million and \$1 million in dedicated ship time.

3.3.4 Deploy moorings and carry out time series studies of pCO_2 and related biogeochemical properties in major biogeochemical provinces of the world's oceans

We recommend time-series studies utilizing both ships and autonomous platforms to characterize seasonal- to decadal-scale variability in ocean biogeochemistry. We urge that, wherever possible, time-series stations supporting CO_2 observations be joint with those of other programs such as CLIVAR (using, for instance, their proposed flux buoys). The time-series stations will provide the time-continuity that is lacking in the decadal surveys and will allow the program to detect changes in the oceanic system as they occur. The proposed observation program must be designed to detect such changes early, allowing response with additional observational assets, surveys, and in-depth process studies.

Continue time-series stations at HOT and BATS (priority 1)

We recommend continued support and augmentation to include autonomous platforms for the two current American time series at Bermuda (BATS) and Hawaii (HOT). This recommendation is based on the fact that these two sites are the most extensively studied and therefore are optimal to field-test the emerging new autonomous technology required for long-term monitoring (see below). This recommendation is in line with the recommendations given by independent advisory panels of the National Science Foundation and NASA. Estimated cost is \$2 million per year (including the cost of mooring).

Continue and formalize equatorial Pacific time series (priority 1)

We recommend that a time-series program be formalized for the equatorial Pacific based on the existing TAO mooring array and the ships servicing these moorings. This regional time-series site builds on the ongoing efforts of PMEL and MBARI for measuring upper ocean CO_2 concentrations and other properties. Implementing this recommendation will come at relatively modest cost because the new CO_2-oriented work can benefit optimally from the existing mooring infrastructure as well as the regular ship-based servicing in place. Estimated cost is \$600,000 per year (for four systems to observe pCO_2 and related properties, excluding the cost of mooring).

Implement time-series sampling in the boreal North Atlantic and North Pacific (priority 2)

We recommend that existing time-series stations in areas critical for detecting and documenting interannual to decadal ocean variability be augmented with CO_2 measurements (see Tables 4-1 and 4-3 in Chapter 4). Two critical areas are the high latitudes of the North Atlantic and North Pacific. In these regions, the dominant modes of extratropical climate variability, such as the Pacific Decadal Oscillation and the North Atlantic Oscillation, are most strongly expressed. A third critical area is the Southern Ocean, for which model simulations indicate high sensitivity to future climate changes.

Our specific selection of sites is based on the expectation that there will be large variations in biological and physical cycles on interannual to decadal timescales. It is also based on resource availability to service the sites and the existence of previous efforts to study the regions. Specifically, for the North Atlantic, we recommend continuing and augmenting the Labrador Sea time-series site Bravo and the Norwegian Sea time-series site Mike, where previous studies revealed large seasonal variations in the euphotic zone (Takahashi *et al.*, 1993). These sites are optimally placed to study the impact of the North Atlantic Oscillation on upper ocean variability in physics, chemistry, and biology. Accordingly, we also recommend the study of ancillary tracers of biogeochemical processes, as for the VOS studies outlined above. Estimated cost is $2 million annually (including the cost of mooring operations). The cost of dedicated ship time is estimated at $1 million per year (for 25 days of operation in each basin).

Implement time-series sites in the Southern Ocean (priority 3)

Toward the end of the plan's 5-year period, when autonomous technology will be more advanced, we recommend extending the existing set of time-series stations into the Southern Ocean, where model simulations clearly indicate the most dramatic long-term changes in response to global climate. Extending observational capabilities into this region is extremely important, since this region is not only sensitive, but represents an area where relatively small climate changes can result in large changes in CO_2 fluxes and ocean storage. Estimated cost is $2 million per year (including the cost of mooring and ship operations). The cost of dedicated ship time (50 days) is estimated at $1 million annually.

3.3.5 Design and implement a data management and access system that will make CO_2 measurements easily accessible on the web, including both discrete data and fields determined using interpolation schemes (priority 1)

The data obtained in this effort will be most useful if it can be provided to the community in a uniform collated format. Rapid dissemination (less than a year) is critical as well so that the data can be used as boundary conditions and constraints for models. Moreover, the data should be available for the

biennial assessment (see Chapter 6). It is critical that this data management system is in place at the time the data is being gathered in the field rather than after the fact. Estimated cost is $400,000 per year.

3.3.6 Develop improved autonomous sensors for sea surface analysis of pCO_2 and related properties

The ability to autonomously measure pCO_2 and other properties of biogeochemical interest will greatly extend our knowledge of air-sea CO_2 fluxes and mediating processes. We recommend the following development efforts to extend these capabilities.

Improve autonomous pCO_2 instruments (priority 2)

We recommend that resources be devoted to a small number of efforts to improve and test instruments for measuring sea surface pCO_2 on VOS, moorings, floats, and drifters. Development efforts should achieve some or all of the following: improving accuracy, durability (and extending the duty cycle), data handling, and ease of use; and lowering costs. We strongly encourage SBIR initiatives to produce pCO_2 systems and other seagoing instruments at competitive cost. Estimated cost is $400,000 annually.

Develop improved sensors for measuring ancillary geochemical properties (priority 2)

Improved sensors should be developed for measuring such ancillary properties as NO_3^-, SiO_2, and DOC. Development of samplers may also be appropriate. We recommend funding projects that show the greatest promise within the available resources. Estimated cost for this effort is $1 million annually.

3.3.7 Develop formalisms for interpolating air-sea CO_2 fluxes in time and space, and seasonal and annual averages, from local flux values (priority 3)

The calculation of air-sea fluxes from sea surface pCO_2 fields, gas exchange parameterizations, and wind speed (or another satellite property) needs to be developed, to calculate the basin-scale flux fields that are the primary product of the recommended observations. Estimated cost is $300,000 per year.

3.3.8 Deploy drifters with pCO_2 sensors to map pCO_2 fields of otherwise inaccessible regions and regions where large seasonal pCO_2 variations are linked to large biogeochemical fluxes (priority 3)

This work has several objectives:

- Map the pCO_2 fields in important regions of the North Atlantic, equatorial and North Pacific, and Southern Oceans that are not accessible by using ships of opportunity.
- Carry out Lagrangian experiments (in which observing platforms move with surface water bodies) to determine timescales of pCO_2 variability at local spatial scales, and distinguish biological and physical influences.
- Acquire a data set to enhance understanding of the information content from a large array of pCO_2 drifters, for planning future observations.

We suggest a series of experiments, addressing the three objectives listed above, involving about 20 drifters. Possible sites and more specific objectives include the following.

Improve knowledge of the pCO_2 field of the Southern Ocean

Drifters released along a meridional line would flow to the east and monitor seasonal changes in pCO_2 and other properties over a broad zonal reach. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

Study the springtime pCO_2 drawdown in the North Atlantic during the bloom

Drifters could be released during springtime, in a grid that would give continuous records of sea surface pCO_2 during the period of the bloom over a large part of the basin. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

Improve knowledge of the synoptic pCO_2 field in the equatorial Pacific

Drifters starting in two N-S lines would flow eastward and westward parallel to the equator, giving a detailed picture of the evolution of regional pCO_2 variations and their relation to mesoscale physics and satellite chlorophyll fields. Estimated costs are $35,000 per drifter plus $25,000 for deployment and data reduction; total estimated costs are $1.2 million. Dedicated ship time has an estimated cost of $1 million, for 50 days.

These three experiments are intended as examples of opportunities, rather than projects specifically recommended for implementation.